***Highlights**

- Simultaneous analyses of BuTs and total Sn enable assessment of TBT long-term behaviour.
- Simultaneous analyses of BuTs and total Sn enable assessment of initial TBT input.
- Sn contamination of coastal environment principally originates from TBT-antifoulings.
- Less than 10% of the initial TBT input reaches sediment before being degraded.
- Contrary to MBT and DBT, TBT remains attached in the sediments during resuspension.

Simultaneous analysis of butyltins and total tin in sediments as a tool for the assessment of tributyltin behaviour, long-term persistence and historical contamination in the coastal environment

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Abstract

This study presents a new approach for the investigation of tributyltin (TBT) behaviour and fate in the marine environment. The approach is based on a simultaneous analysis of butyltins (BuTs) and total Sn in sediments, thus enabling an assessment of its long-term persistence and historical input. The study also presents first evaluation of the extent to which the TBT-antifouling paints contribute to the contamination of coastal environments with inorganic Sn; it was demonstrated that the inorganic Sn in the investigated areas primarily originates from TBT degradation.

The study was conducted by analyzing BuTs and total Sn in sediments from 34 locations along the Croatian Adriatic coast. The results revealed that 85% of the locations were contaminated with both BuTs and inorganic Sn. The share of ΣBuTs/total Sn was low ($<$ 10%) even in sediments with low TBT degradation efficiency (TBT/ΣBuTs $>$ 40%), demonstrating that only small portion of TBT introduced into the water column reached the sediment before being degraded. This means that recent input of TBT into the marine environment may be at least 10 times higher than the amount estimated if only BuTs levels in sediments are considered. It was also demonstrated that TBT concentration in sediments with TOC < 1% is not a good indicator of the overall pollution level, even if TBT/TOC approach is used in pollution assessment. Finally, *in situ* investigation showed that resuspension of contaminated sediments leads to significant release of MBT and DBT into the water column, whereas TBT mainly remains in sediment.

Keywords: tributyltin (TBT), inorganic tin, pollution, sediments, resuspension

1. Introduction

Tributyltin (TBT) has found a wide application as biocide in antifouling paints. Its intensive use started in 1960s and continued for decades until toxicity to various non-target marine organisms was established (Graceli et al., 2013; Omae, 2003). The most severe effect it causes is occurrence of imposex in gastropods at very low concentrations in seawater (1 - 2 ng L^{-1}) (Omae, 2003). For this reason, TBT is declared as one of the most toxic pollutants to be purposely introduced into the marine environment and, consequently, its use in antifouling paints has been banned in many countries worldwide, including all of Europe. The International Maritime Organization (IMO), through establishment of the AFS Convention in 2001, demanded a global ban of these paints all over the world from 2003. The European Union implemented the Convection through the Regulation 782/2003/EC, and the year 2008 was determined as a deadline for the complete removal of old TBT coatings from the ship hulls.

Despite these regulations, literature data clearly demonstrates that TBT pollution is still an important environmental issue, far from being solved even more than a decade after its global ban. Although a decline in TBT levels was observed, both in Europe (Cuevas et al., 2014; Galante-Oliveira et al., 2010, 2011; Guomundsdóttir et al., 2011; Langston et al., 2015; Nicolaus and Barry, 2015; Verhaegen et al., 2012), and worldwide (Castro et al., 2012; Choi et al., 2013), all these studies demonstrated that complete recovery of the marine environment was not achieved because TBT was often found in concentrations above levels toxic to biota. Even recently, high TBT levels were reported in many studies (Anastasiou et al., 2016; Artifon et al., 2016; Batista-Andrade et al., 2018; Erdelez et al., 2017; Filipkowska et al., 2019; Romanelli et al., 2019; Kim et al. 2017, 2017b; Lam et al., 2017; Laranjeiro et al., 2018; Quintas et al., 2016; Ruiz et al., 2017), particularly in countries where the use of TBT-antifouling paints is still not well regulated (Batista et al., 2016; Grimón et al., 2016; Mattos et al., 2017; Paz-Villarraga et al., 2015).

After entering the water column, TBT is subjected to microbiological and photolytic degradation, consisting of a stepwise loss of butyl groups - via dibutyltin (DBT) and monobutyltin (MBT), and finally to inorganic Sn, with half-lives ranging from several days to weeks (Omae, 2003). Given its strong affinity for the adsorption onto the suspended particles, a portion of TBT eventually ends up in sediments, where its degradation continues very slowly, with half-lives from several years to decades (Furdek et al., 2016; Omae, 2003; Viglino et al., 2004). This is why contaminated sediments are considered not only as a long-term reservoir of TBT, but also as a potential source of pollution for the water column once its input through the antifouling paints will be completely terminated. Despite this, the behaviour and persistence of TBT in sediments have not been completely elucidated; meanwhile, in all field research conducted so far, except in two studies where BuTs degradation was investigated using species-specific isotopic tracers (Furdek et al., 2016; Rodriguez-Gonzalez et al., 2013), they have been studied through distribution of only butyltins, namely, TBT and its degradation products - MBT and DBT, but inorganic Sn as the final product of degradation was never considered (Abraham et al., 2017; Almeida et al., 2004; Hartwell et al., 2016;

Sarradin et al., 1995; Scrimshaw et al., 2005), which could potentially affects the conclusions reached.

The inorganic Sn, formed by the TBT degradation, is converted to the insoluble hydroxide specie, $Sn(OH)_4$ (Byrne, 2002), which likely adsorb onto particulate matter, and is rapidly scavenged by particles, whereas subsequent release of inorganic Sn from sediments is unlikely (Howe and Watts, 2005). The study of Langston et al. (1987) confirmed that large proportion of Sn in the water (up to 93%) was present in the particulate form. This means that inorganic Sn formed by the degradation of TBT, either in the water column or in the sediments, will eventually end up retained in sediments. Therefore, we assume that the simultaneous analysis of BuTs and total Sn in sediments could be used as a tool for the investigation of long-term persistence of TBT in sediments, and elucidation of its historical input. Even though this approach should enable a wider understanding and more reliable assessments than the analysis of only BuTs, it was never employed in previous investigations of TBT behavior. Indeed, the relationship between TBT and inorganic Sn in sediments was investigated in only one study (Pougnet et al., 2014).

As a result of degradation, in less than 10 - 12 half-live periods, the inorganic Sn will represent more than 99% of the initial amount of TBT introduced. Consequently, the expected long-term outcome of TBT input into the marine environment are sediments enriched with Sn. Despite this, the inorganic Sn contamination of the marine environment has not received much attention, and it was never demonstrated to which extent TBT-antifouling paints contribute to the contamination of coastal sediments with inorganic Sn.

It is considered that TBT stored in sediments could be released back into the water, particularly due to sediment resuspension (Berg et al., 2001; Hoch and Schwesig, 2004; Ruiz et al., 2008). In fact, BuTs desorption from sediments has been demonstrated in several studies, but these were either laboratory experiments (Berg et al., 2001; Burton et al., 2004; Hoch et al., 2003; Langstone and Pope, 1995), or studies in which diffusion of BuTs from sediments was assessed on the basis of their concentrations in porewater (Burton et al., 2005; Viglino et al., 2004). In several studies the occurrence of imposex or high levels of BuTs in marine organisms were discussed in terms of their release from the contaminated sediments (Laranjeiro et al., 2018; Ruiz et al., 2008). However, field experiments concerning this topic are scarce; only a few studies demonstrated that desorption of BuTs, TBT in particular, from undisturbed sediments is insignificant (Stang and Seligman, 1987; Stuer-Lauridsen and Dahl, 1995). Indeed, *in situ* study strongly confirming to what extent contaminated sediments act as a source of TBT for the water column is still lacking.

This study aims to further explain the fate of TBT upon entering the marine environment; it explores the relationship between the total Sn and BuTs in sediments with the aim to define a new and improved tool for the investigation of TBT behaviour, persistence, and its historical input. Moreover, the study evaluates the risk related to the remobilization of BuTs from contaminated sediments. The specific objectives of this work were: (i) to determine the BuTs and total Sn distribution in coastal sediments along the Croatian Adriatic coast, and to assess the level of TBT pollution following the global ban; (ii) to evaluate the long-term behaviour and persistence of TBT in various sediments using proposed BuTs-total Sn approach; (iii) to investigate the relationship between BuTs and inorganic Sn in sediments with the aim to assess in which extent the TBT-based antifouling paints contribute to the inorganic Sn contamination in coastal areas; (iv) to investigate the BuTs behaviour during resuspension of contaminated sediments.

2. Materials and Methods

2.1. Study area

The investigated area covers the coastal zone of the Croatian Adriatic Sea (Mediterranean Sea). This is densely inhabited area that is also a well-known tourist destination. Along approximately 530 km of coastline are located 41 cities (60 towns with more than 2000 habitats), 106 nautical ports of which 67 are marinas, and five shipyards. This area is under a great anthropogenic influence caused by intense marine traffic, tourism, industry, and urbanization.

2.2. Sampling

Sediment samples were collected at 34 sampling locations along the coast in the period 2010 - 2012 (Fig. S1, in Supplementary Information (SI)). Sampling locations comprises: (i) marinas (M) - areas of heavy boat traffic associated with nautical tourism; (ii) ports - big commercial city ports (P), small local ports (Ps) and shipyards (S); and (iii) reference locations (R) - coastal areas occasionally exposed to marine traffic but without retention of ships, including several locations distant from the shore in deep-water areas (up to 100 m depth). Description of the sampling sites (number of berths, water depth, distance from the shore) is given in Table S1, in SI.

Sediment sampling

Surface sediments (0 - 2 cm) were collected at 34 locations, whereas sediment cores (up to 30 cm depth) were sampled at six locations. In three marinas and one shipyard samples were taken in the vicinity of service hoist (assignment: M-H and S-H, respectively).

Sediments were collected using a gravity corer (Uwitec, Austria) and frozen immediately after the sampling. The sediment cores were cut into 2-cm layers. All samples were freeze-dried and homogenized by milling (except for the grain-size analyses). The samples were kept at -20 °C until analyses.

Sampling of the bottom water

The bottom water, i.e. the water overlaying the sediment surface, was collected at 10 locations using a gravity corer. The corer intrusion into sediment induced a resuspension of fine particles from the sediment surface layer; thus, the overlying water was sampled after these particles had settled down, which was approximately after 15 min. Water from the gravity corer was transferred into dark glass bottles, acidified with HNO_3 to pH of 2 – 3, and stored at 4 °C until analyses.

2.3. BuTs determination in sediments

The BuTs (TBT, DBT, and MBT) were extracted from the sediment by acetic acid and ultrasonic stirring, following the method described in Furdek et al. (2016). The simultaneous derivatization with $NaBEt_4$ and extraction into hexane were performed in a sodium cetate-acetic acid buffer (pH 4.8) by mechanical shaking. The analyses were conducted on the gas chromatograph (GC, Varian CP 3800) with pulsed flame photometric detector (PFPD, Varian). The quality control was performed by the analysis of the standard reference material certified for BuTs in marine sediments (PACS 2, Ottawa, Canada), with the recoveries of all three BuTs being within the certified values. Tripropyltin (TPrT) was used as internal standard, and the results are expressed as ng(Sn)g^{-1} dry weight (d.w.). The detection limits ranged from 0.9 to 6.1 ng(Sn) g^{-1}.

2.4. BuTs determination in seawater

The BuTs in seawater were determined by the method described in Furdek et al. (2012). Briefly, BuTs were extracted from the seawater by mechanical shaking in a sodium acetate-acetic acid buffer (pH 4.8) after the addition of $NaBEt_4$ and hexane. The analyses were performed on a gas chromatograph (GC, Agilent 6890) coupled to inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7900). The quality control was performed by a recovery experiment with known amounts of BuTs. The detection limits ranged from 0.11 to 0.35 ng(Sn) L^{-1}.

2.5. Total tin in sediments

Analyses of the total Sn in sediments were performed by the method described in Sondi et al. (2017), using high resolution inductively coupled plasma mass spectrometry (HR ICP-MS; Element 2, Thermo Finnigan). Briefly, sediments were digested in the microwave oven (Multiwave 3000, Anton Paar) by two-step total digestion procedure; I step: HNO_3 (65% *p.a.*) + HCl (36% *s.p.*) + HF (48% *s.p.*), and II step: H_3BO_3 (40 g L^{-1}). The quality control was performed by the simultaneous measurements of the certified reference materials for marine sediment (MESS-3, NRC, Canada), for which satisfactory results were obtained.

2.6. Total organic carbon (TOC) and the grain size analyses of sediment samples

TOC analyses were performed by the high-temperature catalytic oxidation (HTCO) method with non-dispersive infrared (NDIR) detection on the solid sample module SSM-5000A connected with TOC-V_{CPH} Shimadzu total organic carbon analyser. The inorganic carbonate fraction was removed with 2M HCl, followed by drying at 50°C overnight. The grain size analyses were performed using a laser diffraction particle size analyser LS 13320 (Beckman-Coulter, USA).

3. Results and Discussion

3.1. Butyltins distribution in surface sediments

BuTs were determined in surface sediments at all investigated locations, except at the two sites distant from the shore (R21 and R22) (Fig. 1a). The concentration of total BuTs (ΣBuTs

= MBT + DBT + TBT) varied between 7.9 and 1362 ng(Sn) g^{-1}. The exceptions were samples collected near the service hoists in two marinas (M1-H, M2-H) and the shipyard (S1-H), in which significantly higher (2 to 3 orders of magnitude) concentrations were detected (10,120 - 66,345 ng(Sn) g^{-1}). According to the Norwegian environmental quality classification system for contaminants in sediments, defined for management purpose (Good: 1 - 5; Moderate: 5 - 20; Bad: 20 - 100; Very bad: > 100 ng(TBT) g^{-1}; Bakke et al., 2010), the environmental status of 85% of the investigated locations was evaluated as Bad or Very bad.

The results revealed that TBT pollution of coastal environment is an ongoing environmental issue in Croatia, as was also demonstrated for many environments worldwide (see references in Introduction). This may be because of an on-going illegal use of the TBT-based paints, particularly on small leisure boats. These paints are obviously still available from the old stocks, but can even, despite their restricted sale and production, be purchased in some western countries (Turner, 2014; Sea Hawk Paints website (USA) - accessed March 2020). Another problem could be old TBT coatings that were not properly removed from the hulls, but only covered with a new layer of a TBT-free paint. A recent study performed in Nordic countries demonstrated presence of TBT in the subsurface paint layers of all investigated boats (Lagerström et al., 2017), suggesting that this biocide may be more commonly occurring on leisure boats than generally thought.

The prevailing BuT compound in sediments from marinas and ports was TBT, which generally represents more than 40% of the total BuTs (Fig. 1b). Quantitative evaluation of the degradation efficiency of TBT was performed by calculating the Butyltin Degradation Index (BDI) according to Equation 1; BDI < 1 indicates poor TBT degradation or its recent input, whereas BDI > 1 indicates efficient degradation of TBT, implying its high degradation rate or older input (Diez et al., 2002; Filipkowska et al., 2011).

$$BDI = \frac{(MBT + DBT)}{TBT} \qquad (1)$$

The calculated BDI values in marinas and ports varied between 0.2 and 5.8, with the average of 1.4 ± 1.1, whereas in reference sites BDI ranged from 0.5 to 3.8, with the average of 2.5 ± 1.3 (Fig. 1b). Although samples from reference sites exhibited generally higher BDI values, the difference between polluted (marinas and ports) and non-polluted (reference) sites is smaller than expected given the large discrepancy in the traffic intensity. This indicates that the persistence of TBT in sediments does not primarily depend on the initial level of TBT input, but could be strongly influenced by other parameters, such as sediment characteristics.

To evaluate the influence of sediment characteristics on BuTs behaviour in sediments, we performed TOC and grain size analyses, and these results are presented in Fig. 2a. The TOC content ranged from 0.35 to 5.65%, with the average of 2.43 ± 1.33%. The grain size analyses showed predominance of the silt fraction (2 - 63 µm) in most samples, ranging from 24 to 80%, whereas the share of clay fraction (< 2 µm) varied between 5 and 22%. According to the Shepard´s classification (Shepard, 1954) sediments were defined as clayey and sandy silts, and silty sands (Fig. 2b).

No correlation was found between the concentrations of BuTs and the share of different sediment fractions, either with the fraction < 2 µm or with the fraction < 63 µm. Additionally, no difference in level of pollution among clayey and sandy silt sediments was observed; but, sediments classified as silty sands, with more than 50% of sand fraction, exhibited low concentrations of TBT (< 50 ng(Sn) g^{-1}; M1-1, M9, Ps5, R6; Fig. 2b). On the other hand, TOC exhibited statistically significant positive correlation with both TBT and total BuTs (r = 0.53, r = 0.48, respectively; Spearman, $p < 0.01$), which is in agreement with the data from other studies demonstrating the important role of organic matter in the adsorption of BuTs onto the sediments (Batista et al., 2016; Berg et al., 2001; Filipkowska et al., 2014; Hoch and Schwesig, 2004). But, the significant correlation was established between the share of TBT (%TBT) and TOC, and between BDI and TOC as well (Spearman; r = 0.41, r = -0.42, respectively; $p < 0.05$), indicating that sediments with higher TOC content have more non-degraded TBT. These results further support the conclusion of our previous investigation in which was demonstrated that organic matter in sediments influences not just the adsorption of TBT but also its degradation efficiency, leading to higher TBT persistence in sediments with higher organic matter content (Furdek et al., 2016).

Thus, when evaluating the TBT pollution level or its persistence in a certain environment, the TOC content should be taken into account; normalization of TBT concentrations to TOC (TBT/TOC ratios) may prevent false assessment that could be made if only TBT levels are considered. In this study, TBT/TOC approach revealed similar pollution assessment for most locations, but several locations where TOC in sediments was < 1% (M1-1, M5-1, M5-2, M6-2, M7, M15, and Ps5) were evaluated as significantly more polluted (Fig. 1a). High TBT pollution at these locations was additionally confirmed by high levels of TBT determined in seawater and mussels during the same sampling campaign (Furdek et al., 2012).

To further explore the difference in TBT pollution assessment using these two approaches, the one that is based on only TBT levels and the other that recommends including the TOC content (TBT/TOC ratios), we gathered literature data on the TBT concentration and TOC content in surface sediments from 10 different studies (Fig. 3). A significant correlation was established between the TBT concentrations and TBT/TOC ratios (Spearman, $r = 0.79$, $p < 0.05$; Fig. 3a). While this confirms that the TBT levels in surface sediments are controlled by the organic matter content, it also suggests that both approaches agree in their pollution assessment for most locations. But, as shown in Fig. 3a, some data are widely dispersed above the TBT - TBT/TOC regression line, and all correspond to sediments with TOC < 1%; therefore, the correlation is much stronger if these data are excluded (Fig. 3b; Spearman, $r = 0.96$, $p < 0.01$). This demonstrates that sediments with TOC < 1% may not provide a reliable pollution assessment reflecting true TBT pollution level in a certain environment using either of the two approaches. These sediments have limited capacity for retaining TBT even if significant pollution is present in the water column, whereas the use of TBT/TOC ratios could lead to the overestimation of the pollution level.

3.2. Relationship between BuTs and total tin in surface sediments

The concentrations of total Sn in the surface sediments are presented in Fig. 4. In most samples Sn concentrations varied from 1.5 to 20 μg g^{-1}, and were roughly in the range found in other coastal areas (Almeida et al., 2004; Babu Rajendran et al., 2001; Hartwell et al., 2016; Pougnet et al., 2014; Sondi et al., 2017). The proportion of BuTs in total Sn (ΣBuT/total Sn) was low in most surface sediments, and ranged from 0.2 to 24.8%, rarely exceeding 10% (Fig. 4); the same was also reported in only few available studies (Hartwell et al., 2016; Pougnet et al., 2014). The exceptions were sediments sampled near the service hoists (M1-H, M2-H, B1-H) with much higher Sn concentrations, ranging from 30 to 110 μg g^{-1}, in which BuTs accounted for 35 - 80% of the total Sn. At almost all of the locations the concentrations were higher than the average Sn level in the upper continental crust (2.5 μg g^{-1}; Wedepohl, 1995) or shale (3 μg g^{-1}; Turekian and Wedepohl, 1961).

The degree of contamination by inorganic Sn was assessed by calculating the enrichment factor (EF) according to Equation 2, whereas aluminium was used as the normalizing element (concentrations of Al are given in Fig. S2, in SI). The background ratio ($(Sn/Al)_{background}$) for the Adriatic coastal sediments was estimated to $5x10^{-5}$, according to the available data (Fiket at al., 2017; Ivanić et., 2017; Mikac et al., 2011; Sondi et al., 2017). The evaluation of the contamination level was performed according to the five-category ranking system; EF < 2 indicates no or minimal, EF = 2 - 5 moderate, EF = 5 - 20 significant, EF = 20 - 40 very high, and EF > 40 extreme enrichment or contamination (Sutherland, 2000).

$$EF = \frac{(Sn_{total}/Al_{total})_{sample}}{(Sn_{total}/Al_{total})_{background}} \qquad (2)$$

The calculated EF (Fig. 4) revealed that almost all sediments were enriched in Sn; 77% of locations were evaluated as moderately or significantly contaminated, whereas areas near the service hoists in marinas and shipyards were assessed as very highly or even extremely contaminated (13%). The assessment of Sn contamination is therefore very similar to the assessment of BuT pollution; in both cases more than 85% of the locations were evaluated as contaminated. Moreover, similar distribution pattern of inorganic Sn and BuTs was observed; sediments from marinas and ports had similar concentrations of Sn, which were, in general, higher compared to the reference sites (Fig. 4). This finding indicates their common source, which is further supported by the significant correlation established between BuTs and inorganic Sn (Spearman, $r = 0.67$, $p < 0.01$).

3.3. The assessment of $Sn_{inorganic}$ origin using modified BDI approach

To investigate in which extent the inorganic Sn in the investigated coastal environments originates from the TBT-antifouling paints, we studied the relationship between TBT and its degradation products (DBT, MBT, and $Sn_{inorganic}$) i.e. BDI. For this purpose, we used a modified approach for BDI calculations (BDI_{mod}, Equation 3) proposed by Pougnet et al. (2014), which, unlike the commonly used BDI expression (Equation 1), takes into account the inorganic Sn as the final product of degradation ($Sn_{inorganic.BT}$).

$$BDI_{mod} = \frac{\left(MBT + DBT + Sn_{inorganic.BT}\right)}{TBT} \qquad (3)$$

The inorganic Sn could enter the marine environment by various sources other than TBT-antifouling paints; municipal and industrial wastewaters as well as landfill leachates. Namely, Sn is used in products such as food cans, welding, electronics, and household products (Howe and Watts, 2005; Pougnet et al., 2014), whereas the input of other organotin compounds, which are widely used as various pesticides and PVC stabilizers, eventually results in the formation of inorganic Sn (Omae, 2003). Therefore, $Sn_{inorganic.BT}$ fraction that derives from the degradation of TBT could be only a part of the whole $Sn_{inorganic}$ calculated as Sn_{total} – $Sn_{background}$. But, in the environments where the entire fraction of the anthropogenic $Sn_{inorganic}$ originates from TBT-antifouling paints, i.e. from the degradation of TBT ($Sn_{inorganic.BT}$ = $Sn_{inroganic}$ = Sn_{total} – $Sn_{background}$ - ∑BuT), the expression for BDI_{mod} given in Equation 3 could be written as:

$$BDI_{mod} = \frac{Sn_{total} - Sn_{background} - TBT}{TBT} \qquad (4)$$

First, we will test the applicability of the BDI_{mod} approach in the assessment of $Sn_{inorganic}$ origin by studying the relationship between TBT and BDI_{mod} in the sediment cores from polluted marinas (M4-3, M10-1, M12, M1-H, M2-H, and B1-H) because we assume that the whole fraction of the anthropogenic Sn in these sediments originates from TBT-antifouling paints. Considering a similar Sn background throughout each sediment core, we omitted the subtraction of $Sn_{background}$ in Equation 4. The stronger correlations between TBT and BDI_{mod} (Equation 4) than between TBT and the classical BDI (which do not take into account the $Sn_{inorganic}$ as the final product of TBT degradation; Equation 1) is established in each investigated sediment core (Fig. S3, in SI), thus confirming that inorganic Sn in the investigated sediments derives from the TBT degradation i.e. TBT-antifouling paints.

We then applied the BDI_{mod} approach to all surface sediments. We did not have data for the background Sn concentrations for all investigated locations, but we assumed that the subtraction of $Sn_{background}$ in Equation 4 could be omitted without compromising the final results and conclusion because we consider that the background Sn level should be similar within the investigated area (according to the available data), whereas the calculated EFs showed that sediments from 90% of the locations were enriched with Sn. Much stronger correlation between TBT and BDI_{mod} (Spearman, $r = 0.85$, $p < 0.01$; Fig. S4, in SI) than between TBT and classical BDI (Spearman, $r = 0.50$, $p < 0.05$; Fig. S4, in SI) indicates that the inorganic Sn has been initially introduced as TBT at most locations. Therefore, we concluded that the inorganic Sn contamination of the investigated coastal area primarily originates from TBT-antifouling paints, not from other potential sources. It follows that the analysis of total Sn in sediments from such locations could give an insight into the initial and historical input of TBT.

3.4. Historical records of BuTs and total Sn in sediment cores – the assessment of long-term behaviour of TBT in sediments

Assuming that i) the inorganic Sn formed by the TBT degradation, either in the water column or in the sediments, eventually ends up retained in sediments, and ii) that inorganic Sn at the investigated locations primarily originates from the degradation of TBT, we hypothesize that the simultaneous analysis of BuTs and total Sn could be a tool for the assessment of long-term behaviour of TBT in sediments and its historical input into a certain environment. We tested this hypothesis by studying the relation between BuTs and total Sn in the sediment cores from six locations (Fig. 5). In three of these cores (M4-3, M10-1, and M12), the degradation efficiency of TBT was already assessed on the basis of only BuTs depth distributions; these results are presented in Furdek et al. (2016) but will be here briefly summarized for the purpose of their comparison with the analysis of total Sn performed in this study.

The total Sn depth distribution in the sediment core M10-1 indicates that this marina was subjected to a constant TBT input over the last decades; the average Sn concentration throughout the core is 17.5 ± 2.8 μg g^{-1}, whereas all sediment layers are significantly enriched with Sn (EF = 11 – 15). Nevertheless, the concentration of each BuT specie and the proportion of TBT/ΣBuTs decreased with depth (from 700 to 10 ng(Sn) g^{-1}, and from 50 to 20%, respectively), whereas BDI > 1 throughout the entire core (Fig. 5a,b,c). This indicates efficient degradation of TBT in this sediment, which is further confirmed by the Sn distribution profile; the share of ΣBuTs/total Sn decreased from 5% in the surface layer to 1%

at the bottom (Fig. 5b), demonstrating that TBT, despite its continuous input, was almost totally degraded to inorganic Sn over time.

On the other hand, in the sediment M4-3 low degradation efficiency of TBT could be assessed on the basis of high proportion of TBT/ΣBuTs (~ 60%) and BDI < 1 throughout the entire core (Fig. 5b,c). Given only BuTs distributions, one might assume that the noticeable decrease of TBT concentrations in the upper part of the core (0 – 6 cm; from 800 to 300 ng(Sn) g^{-1}) reflects TBT input rather than its efficient degradation. But, the total Sn distribution deny such conclusion because the Sn concentrations were consistent with depth implying continuous TBT input (average is 6.7 ± 1.5 µg g^{-1}; EF = 3 – 5; Fig. 5a), whereas the decrease of ΣBuTs/total Sn from 20 to 5% in the upper layers revealed that the decline of TBT concentrations is the result of efficient TBT degradation. At the same time, the proportion of each BuT species was similar as in the deeper layers, indicating that TBT was degraded completely to inorganic Sn.

In the sediment core M12 the concentrations of TBT were high throughout the entire core (450 – 1650 ng(Sn) g^{-1}), as well as the proportions of TBT/ΣBuTs (60 – 80%), indicating extensive TBT input and its high persistence in this sediments (Fig. 5a,b). Both are confirmed by the total Sn distribution; all sediment layers were significantly enriched with Sn (EF = 10 – 14; average is 20.6 ± 2.8 µg g^{-1}), whereas the proportion of ΣBuTs/total Sn was ~ 5% throughout the entire core.

In the sediment cores M1-H, M2-H and S1-H the distribution of BuTs is much different compared to the sediments described above; the concentrations of both BuTs and total Sn were 2 - 3 orders of magnitude higher than in the sediments M10-1, M4-3 and M12 (Fig. 5a; the average is 11 - 55 µg(Sn) g^{-1} for ΣBuTs, and 16 – 83 µg g^{-1} for total Sn; EF = 20 – 80; very high or extreme enrichment). Although noticeable decline of both BuTs and total Sn with depth could be observed (Fig. 5a), the proportion of non-degraded TBT was high throughout all three cores (TBT/ΣBuTs = 50 – 80%; Fig. 5b). Given much higher share of ΣBuTs/total Sn

(20 - 85 %) compared to other sediment cores, and the fact that these samples were collected in the vicinity of service hoists, it is reasonable to conclude that determined TBT and Sn distributions are a consequence of the presence of antifouling paint particles in these sediments. In such sediments, TBT has limited ability to degrade; however, noticeable decline of ΣBuTs/total Sn with depth in the core M1-H indicates that even in those sediments TBT will eventually degrade.

Moreover, similar proportion of non-degraded TBT in these three sediment cores containing paint particles (M1-H, M2-H and S1-H) and those sediments in which high TBT persistence was observed (M4-3 and M12) (TBT/ΣBuTs = 50 - 80%; Fig. 5b) indicates that the leaching rate from the paint matrix is not a limiting step in determining TBT persistence in sediments in which it is mostly present in the form of paint particles. Accordingly, Turner (2010) claims that leaching of biocide from the paint particles can be more intensive than from the painted boat surface because of the greater surface area, particularly in marine sediments containing high salinity pore waters with often low pH values.

In conclusion, the above discussion clearly demonstrates that the simultaneous analysis of BuTs and total Sn in sediments, compared to the analysis of BuTs alone, leads to deeper understanding and more reliable assessments of TBT behaviour and persistence over time, as well as its initial and historical input. Indeed, it was shown that assessments based on only BuTs distribution could lead to false conclusions.

3.5. The assessment of former TBT input and fate using recent sediments

If the entire fraction of anthropogenic inorganic Sn is originating from TBT, the fact that the total Sn concentrations in surface sediments are 10 - 70 times higher than the BuTs concentrations indicates that the overall input of TBT in the last few years was at least 10 times higher than the quantity which may be estimated from the determined BuTs levels in sediments. However, the question is why BuTs account for only less than 10% of the total Sn if degradation rate of TBT in sediments is slow ($t_{1/2}$ = several years to decades; Omae (2003)). In Fig. 6 is clearly illustrated that the share of ΣBuTs/total Sn is less than 10% in almost all surface sediments, even in those in which the proportion of TBT/ΣBuTs is high (> 40 %). A few samples exhibiting higher ΣBuTs/total Sn ratios (20 - 80%) were those taken near the service hoists where most of the TBT arrives to sediments in the form of paint particles.

Given the slow degradation of TBT in sediments, low share of ΣBuTs/total Sn (< 10%) indicates that most of the TBT leached from the ship hulls is completely degraded to inorganic Sn already in the water column, with only a small portion (~ 10%) reaching the sediment in the form of TBT. This is explained by high degradation rate of BuTs in the water column ($t_{1/2}$ = several days to weeks; Omae, 2003), especially in the euphotic zone exposed to intense sunlight where photolytic degradation occurs (Rodriguez-Gonzalez et al., 2013), as was the case in our study (water depth at most locations was < 20 m; Table S1, in SI). The inorganic Sn compounds formed by the degradation are insoluble in water (Byrne, 2002), and are likely to adsorb onto particulate matter (Howe and Watts, 2005); thus, the inorganic Sn formed by the TBT degradation in the water column could be almost quantitatively deposited into the sediments.

3.6. The desorption of BuTs during resuspension of contaminated sediments

To investigate the behaviour of BuTs during the disturbance of contaminated sediments, we analysed the water overlaying the sediment in the gravity corer after the sediment sampling (Fig. 7). The intrusion of the gravity corer into the sediment induced a resuspension of fine particles from the sediment surface, thus somehow imitating the resuspension of sediments caused by some environmental action such as bioturbation or waves.

The concentrations of MBT and DBT in the overlying waters were similar, ranging from 20.7 to 247.5 ng(Sn) L^{-1} for MBT, and from 20.0 to 263.2 ng(Sn) L^{-1} for DBT. These concentrations were considerably higher (up to 200 times) compared to those measured in surface waters at the same locations during the same sampling campaign (MBT ranged from 0.75 to 5.06 ng(Sn) L^{-1}, and DBT ranged from 0.62 to 13.9 ng(Sn) L^{-1}; Furdek et al., 2012). On the contrary, TBT concentrations ranged from 0.71 to 12.4 ng(Sn) L^{-1}, and were significantly lower (10 - 250 times) compared to the concentrations of MBT and DBT, but were similar to those of TBT measured in surface waters (0.39 - 18.2 ng(Sn) L^{-1}; Furdek et al., 2012).

These results demonstrate that BuTs efficiently desorb from sediments during the sediment resuspension caused by the intrusion of gravity corer; however, TBT behaves differently from MBT and DBT desorbing from sediments in a considerably lower extent. Even though TBT was generally the most abundant BuT specie in surface sediments (TBT/ΣBuTs > 40%; Fig. 1b), the proportion of TBT/ΣBuTs in the overlying waters was significantly lower (4 ± 3 %) compared to proportion of MBT (53 ± 8 %) and DBT (43 ± 8 %) (Fig. 7b). This is explained by the fact that TBT, as the most hydrophobic compound, strongly binds to organic matter in sediments, whereas less substituted and less hydrophobic BuTs, because of their weaker adsorption on the sediment particles, more readily desorb from sediment (Hoch et al., 2003). The amount of each BuT compound released is proportional to its concentrations in the surface sediments, as was demonstrated by strong correlations between the overlying waters and surface sediments established for each BuT specie (Fig. S5, in SI; Pearson; $p < 0.01$; MBT: $r = 0.86$, DBT: $r = 0.86$, TBT: $r = 0.91$).

The BuTs distribution determined in the waters overlying the sediment after resuspension could be a result of either the diffusion of pore waters containing BuTs or BuTs desorption from sediment particles upon resuspension. The former is less probable because the BuTs concentrations determined in the pore waters isolated from the contaminated sediments during the same sampling campaign were low (< 10 ng(Sn) L^{-1}) (Furdek at al., 2016), as was also reported in other studies for BuTs in pore waters of sediments having similar level of BuTs contamination (< 10 ng(Sn) L^{-1}; Berg et al., 2001, Viglino et al., 2004).

Conclusions

The presented results allow as to conclude: (i) that the simultaneous determination of both BuTs and total Sn in sediments should be performed to assess the long-term behavior, persistence and input of TBT into the marine environment; the assessments based on only BuTs distribution, as has be done so far, could lead to false conclusions; (ii) TBT input via antifouling paints resulted in high enrichment of coastal sediments with inorganic Sn; indeed, the Sn contamination of the investigated locations completely originates from TBT-antifouling paints; (iii) only a small portion of TBT introduced into the water column (~ 10%) reaches the sediment before being degraded; therefore, the overall input of TBT into the marine environment may be underestimated (at least 10 times) if only BuTs levels in sediments are considered in the pollution assessment; (iv) the resuspension of contaminated sediments leads to a significant release of MBT and DBT into the water column, leaving TBT stored in sediments; (v) the TBT level in sediments with TOC < 1% is not a reliable indicator of the overall pollution of a certain area with TBT, even when TBT/TOC approach is used in the pollution assessment.

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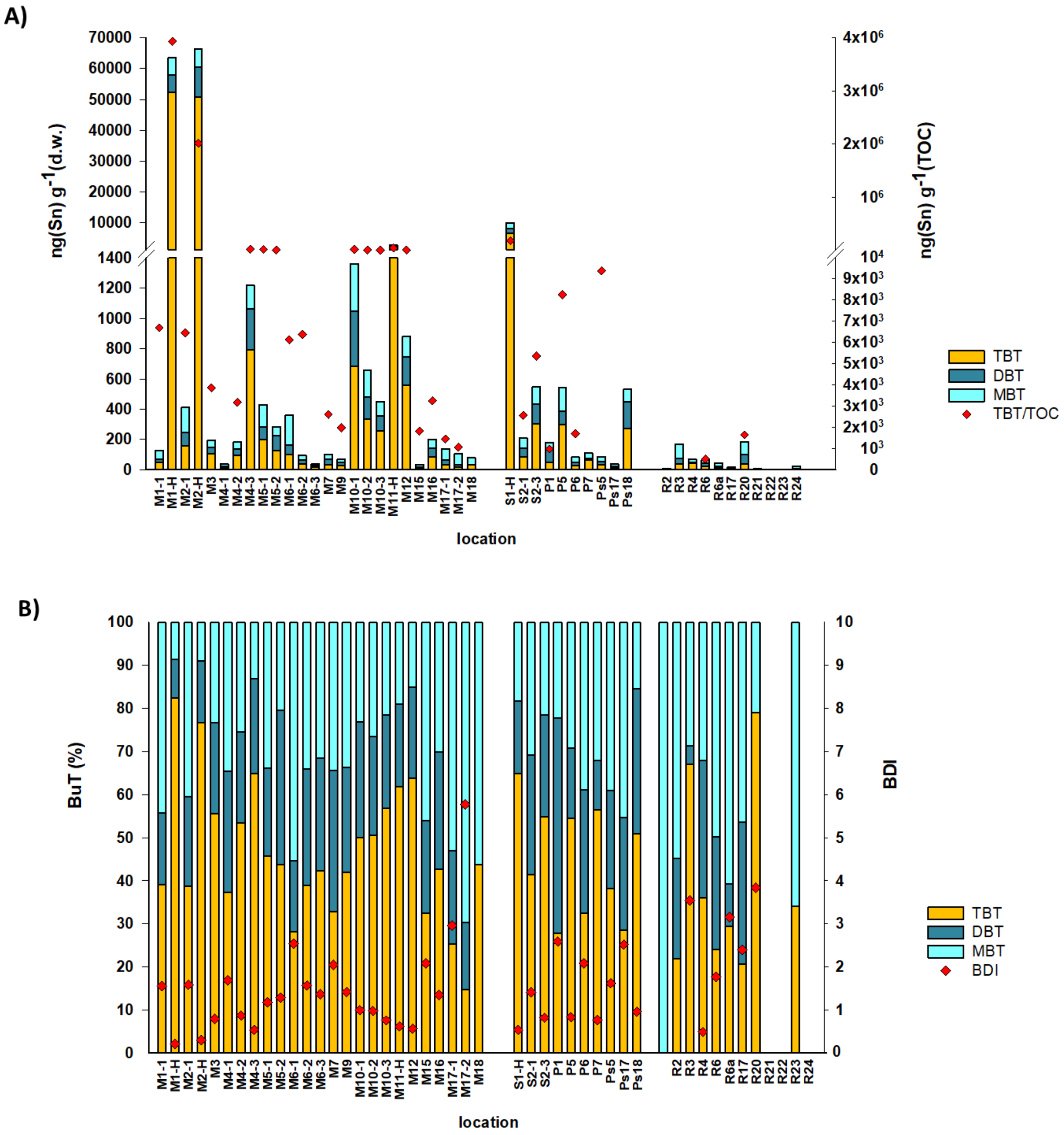


Fig. 1. Butyltin species in surface sediments: (**a**) MBT, DBT and TBT concentrations (ng(Sn) g^{-1}(d.w.)) and TBT concentrations normalized to TOC content (ng(Sn) g^{-1}(TOC)) and (**b**) percentage of each BuT specie in the total BuTs (ΣBuTs) along with the calculated BDI values (BDI= (MBT+DBT)/TBT).

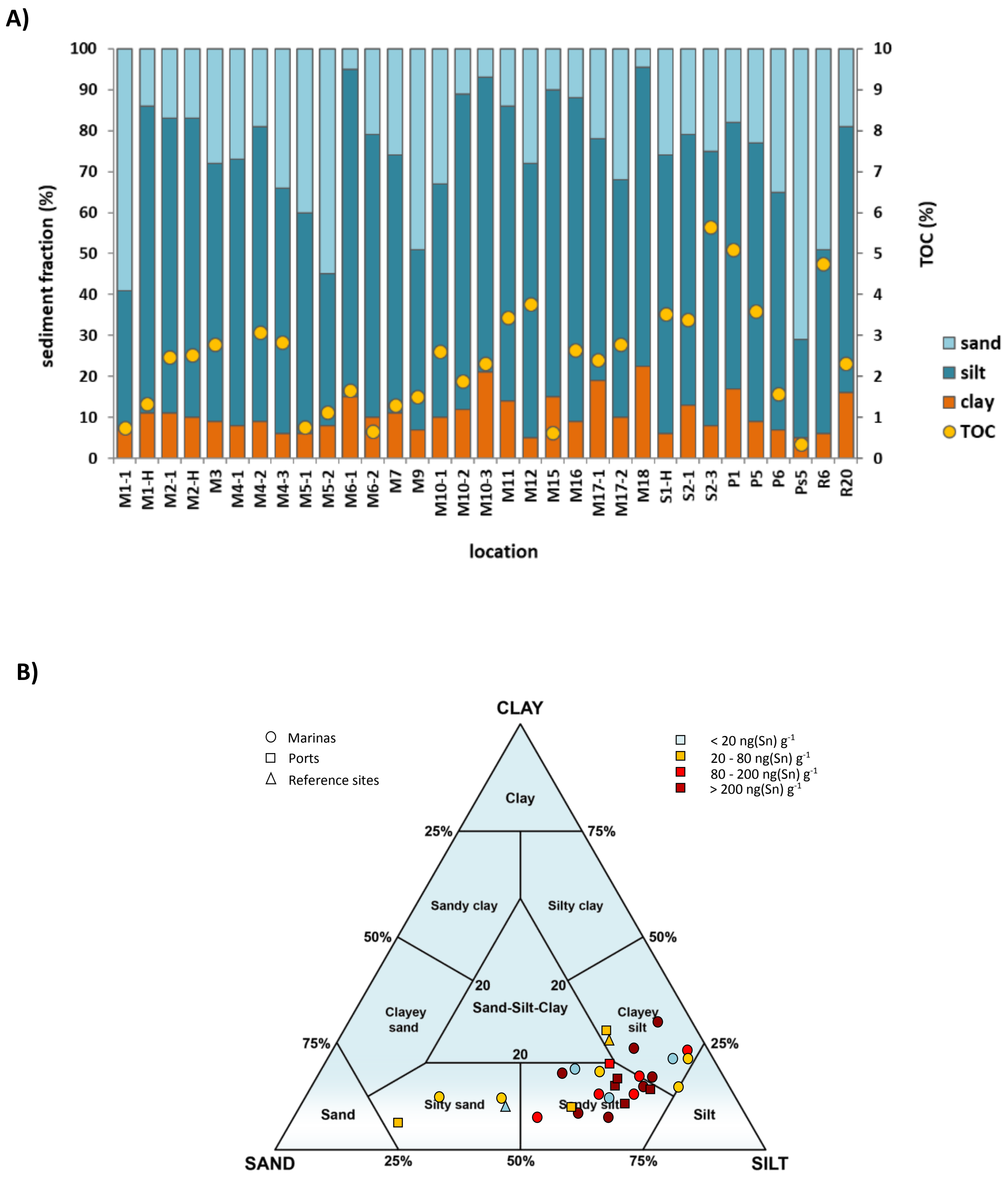


Fig. 2. The distribution of clay (<2 µm), silt (2-63 µm) and sand (63 µm - 2 mm) content and total organic carbon (TOC) in surface sediments (**a**), and the Shepard´s classification of surface sediments (**b**).

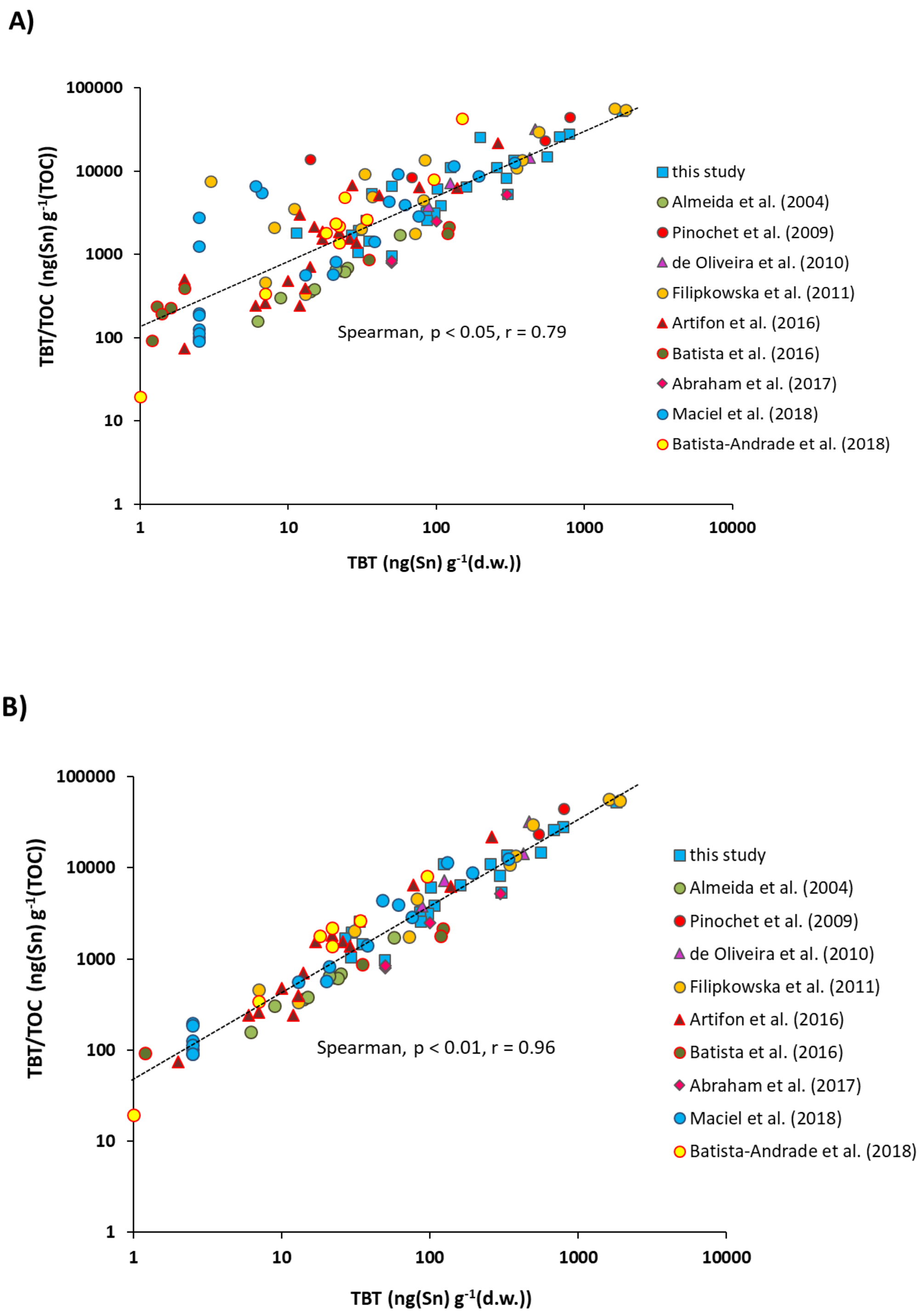


Fig. 3. The relation between the TBT concentrations expressed as ng(Sn) g^{-1}(d.w.) and normalized to TOC content (ng(Sn) g^{-1}(TOC)) in surface sediments gathered from 10 different studies (**a**), and when sediments with TOC < 1% were disregarded (**b**).

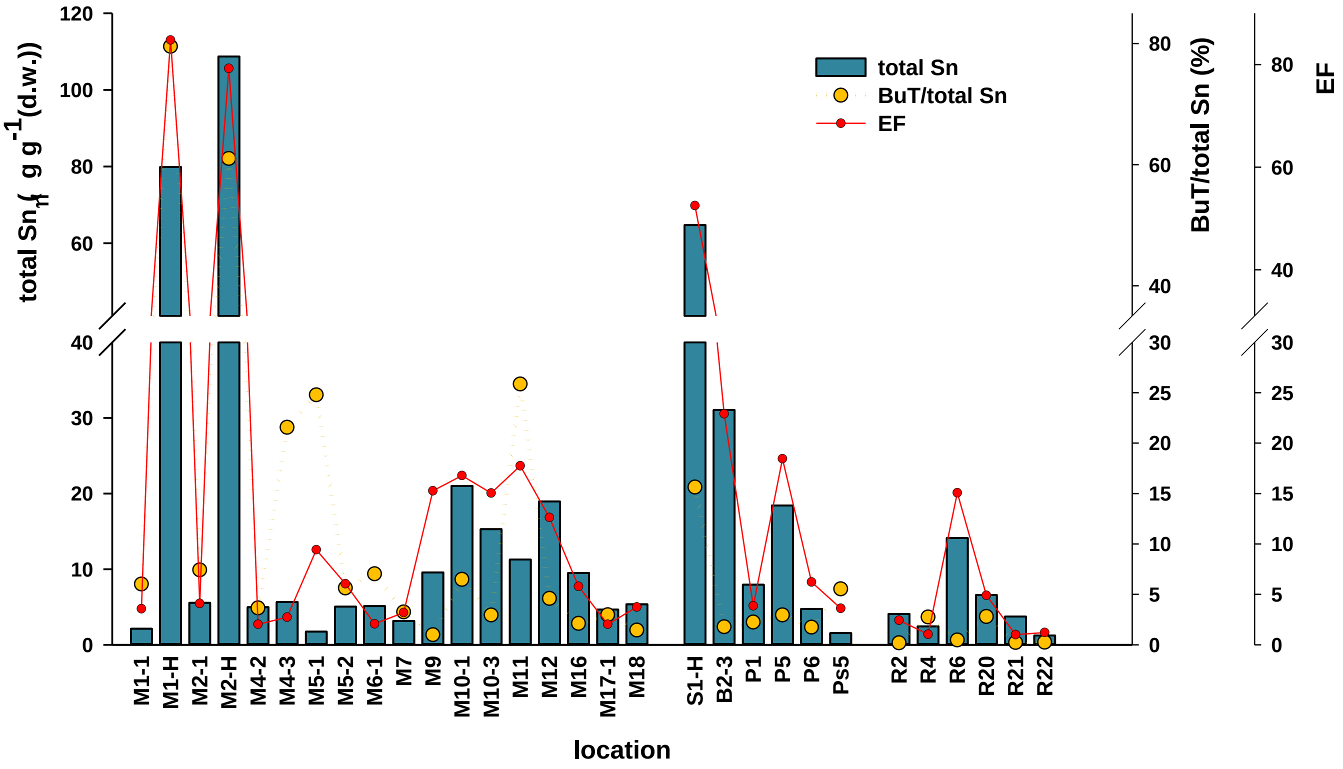


Fig. 4. The distribution of total Sn in surface sediments with the accompanying enrichment factors (EF) and the proportion of ΣBuTs/total Sn.

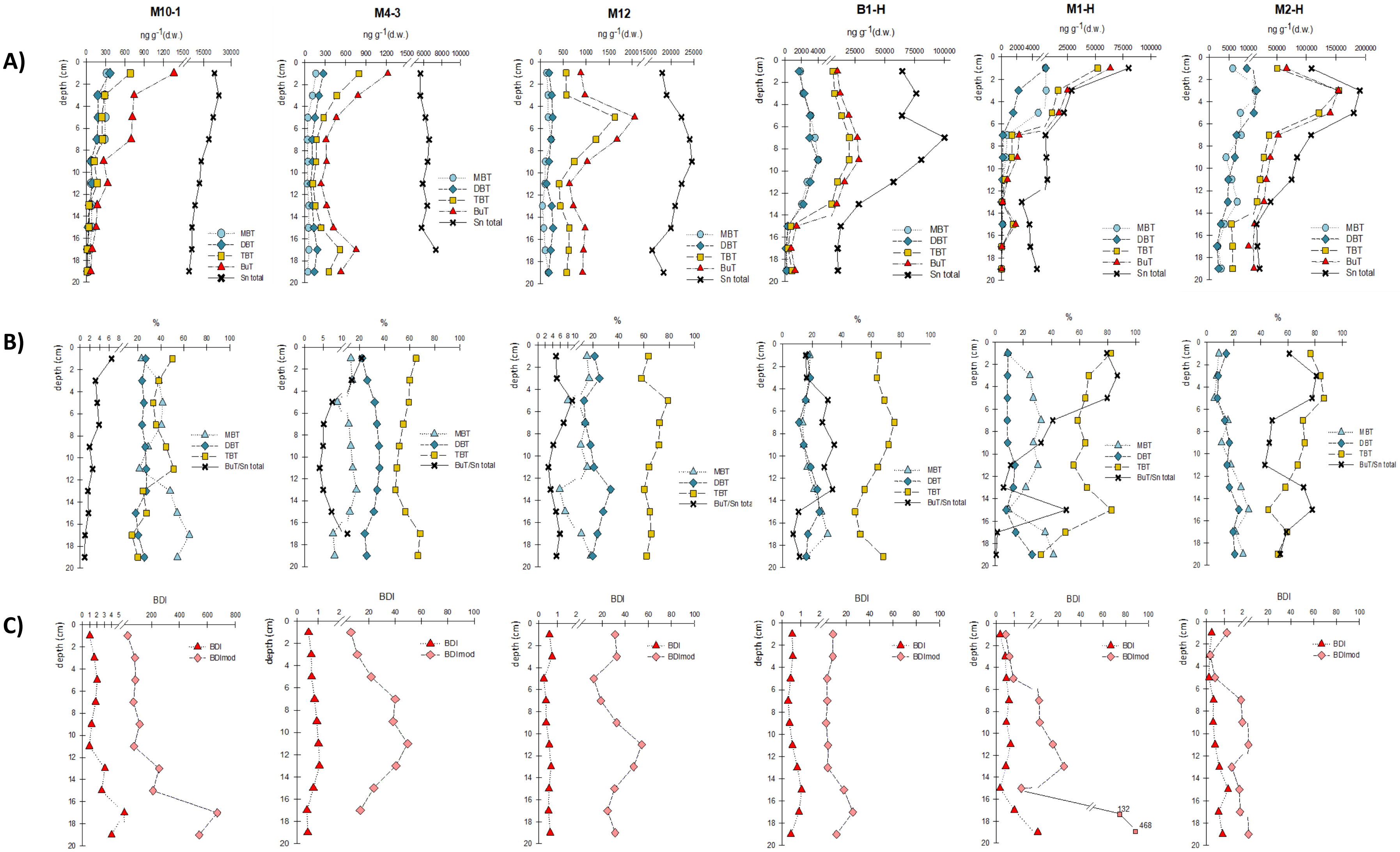
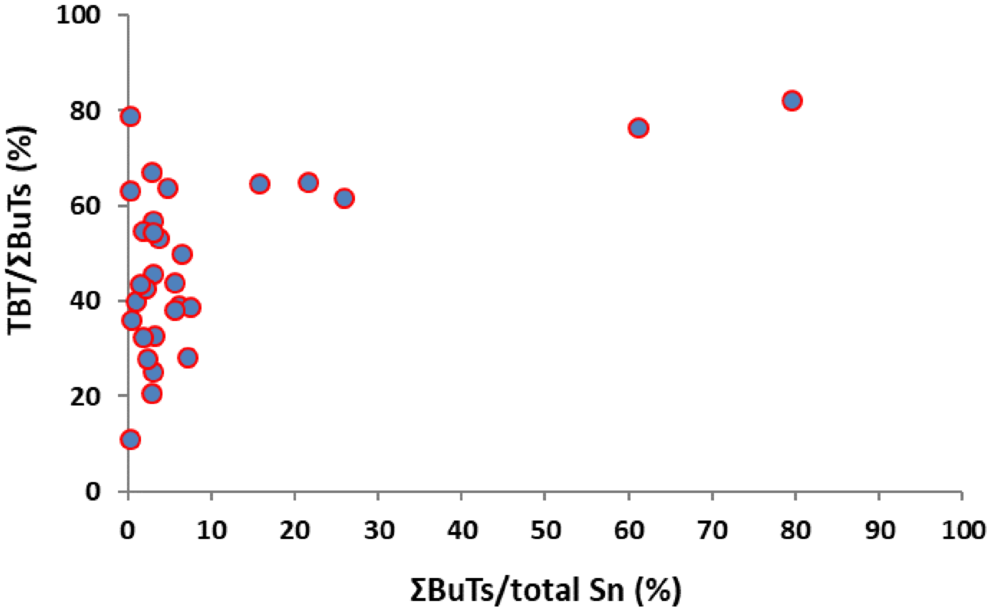


Fig. 5. The vertical distributions of BuTs and total Sn concentrations **(a)**, the percentage of each BuT species in the total BuTs (ΣBuTs) and the sum of BuTs in the total Sn (ΣBuTs/total Sn) **(b)** and BDI and BDI$_{mod}$ in sediment cores **(c)**.
(BuTs distribution in the sediment cores M10-1, M4-3 and M12 are already published in our previous research (Furdek et al., 2016), but are here presented for the purpose of comparison with the total Sn profiles)



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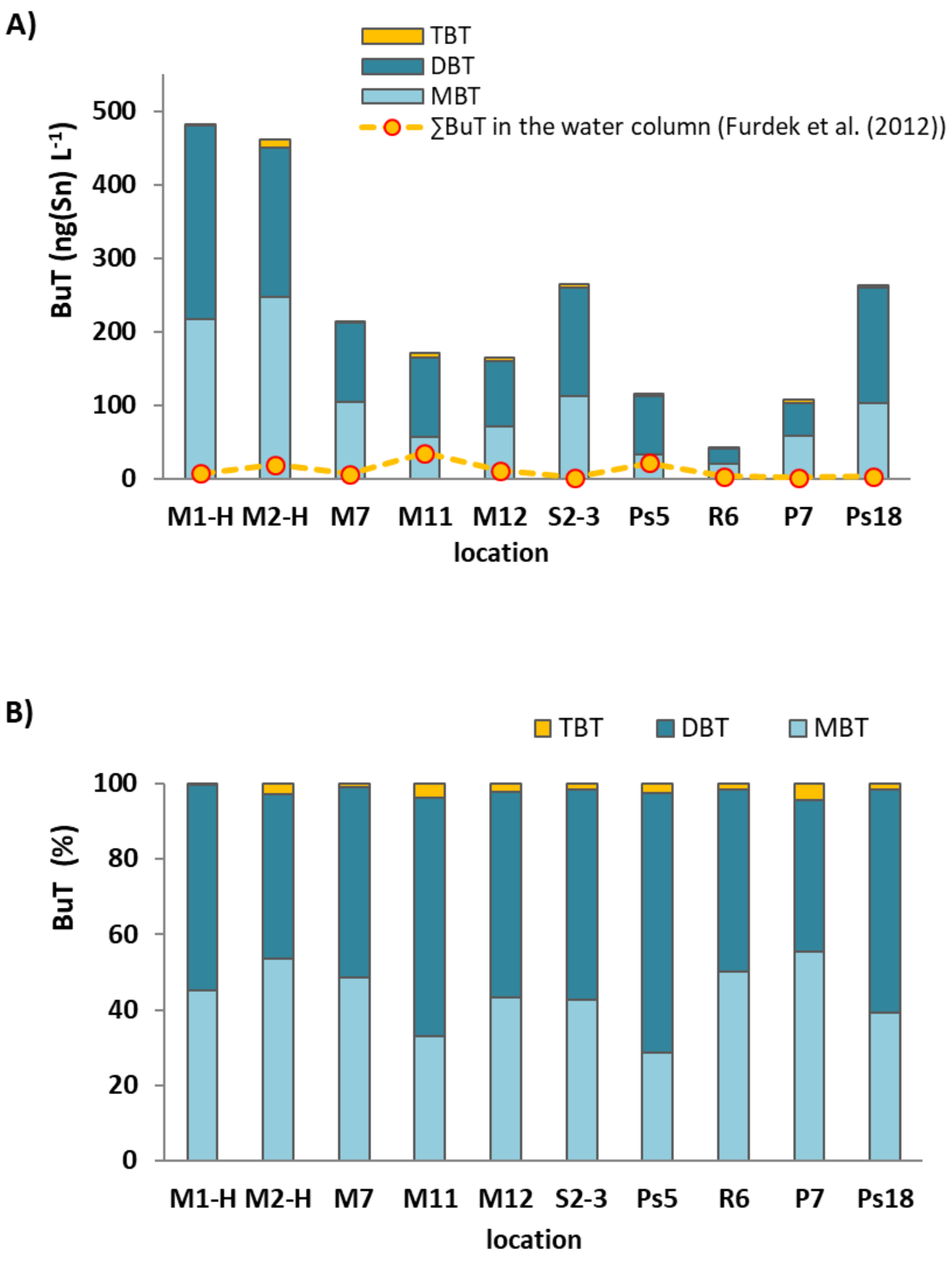

Fig. 7. The concentrations of BuTs **(a)** and the percentage of each BuT specie **(b)** in the waters overlying the sediment after the sediment resuspension.

Figure captions

Fig. 1. Butyltin species in surface sediments: (**a**) MBT, DBT and TBT concentrations (ng(Sn) g^{-1}(d.w.)) and TBT concentrations normalized to TOC content (ng(Sn) g^{-1}(TOC)) and (**b**) percentage of each BuT specie in the total BuTs (ΣBuTs) along with the calculated BDI values (BDI= (MBT+DBT)/TBT).

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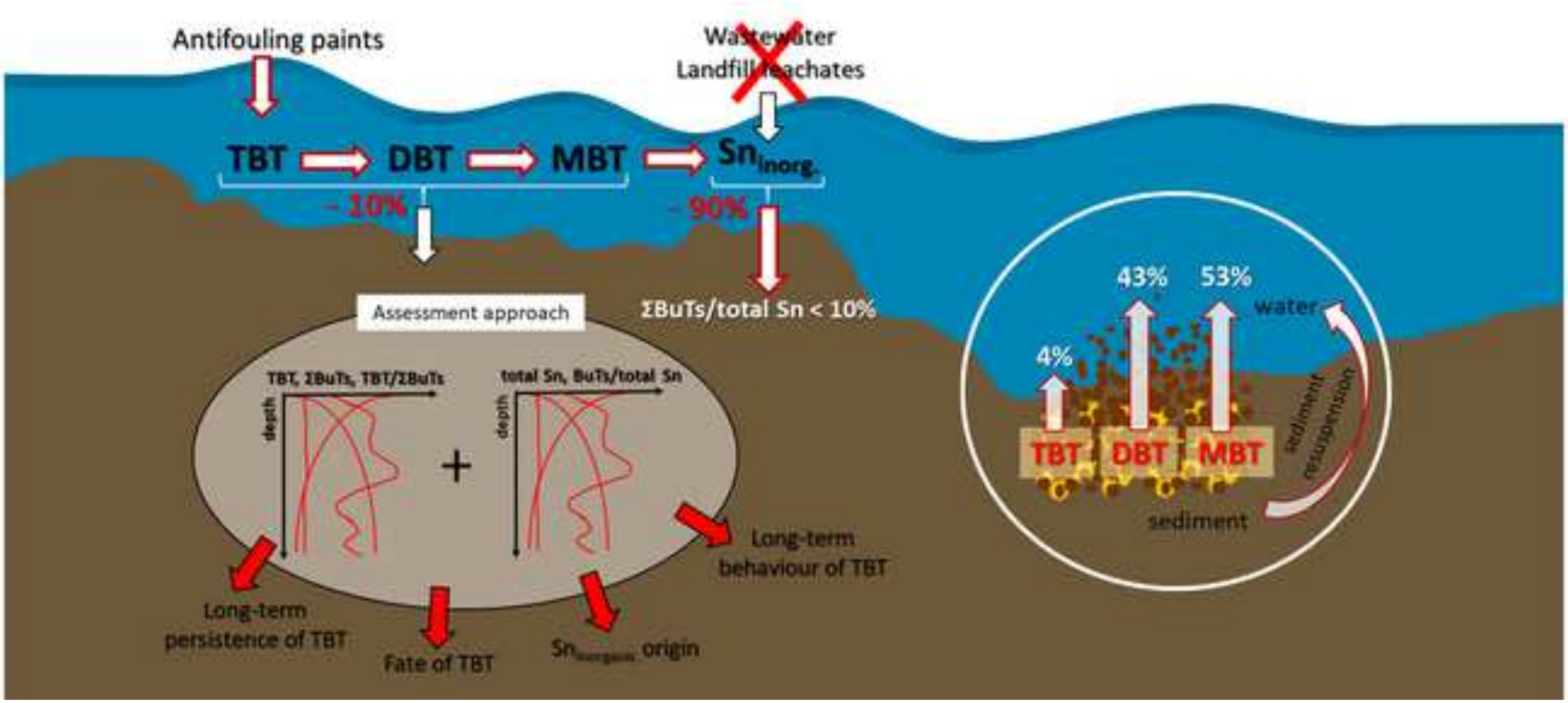
Fig. 7. The concentrations of BuTs **(a)** and the percentage of each BuT specie **(b)** in the waters overlying the sediment after the sediment resuspension.

Graphical Abstract



*Declaration of Interest Statement

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: